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SELECTIVE FLUORINATION OF DISPIRO[3.1.3.1]DECAN-5,10-DIONE BY DIETHYL-AMINOSULFURTRIFLUORIDE TO GIVE 10,10-DIFLUORODISPIRO[3.1.3.1]DECAN-5-ONE AND 5,5,10,10-TETRAFLUORODISPIRO[3.1.3.1]DECANE

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SUMMARY

Dispiro[3.1.3.1]decan-5,10-dione was selectively difluorinated at room temperature by diethylaminosulfur trifluoride (DAST) to give 10,10-difluorodispiro[3.1.3.1]decan-5-one. The latter was reduced to 5,5-difluorodispiro[3.1.3.1]decane and also reacted with excess DAST to give 5,5,10,10-tetrafluorodispiro[3.1.3.1]decane. Proton and fluorine magnetic resonance studies on 5,5-difluorodispiro[3.1.3.1]decane did not show significant cross-ring coupling (< 0.5 Hz) between geminal fluorines on C-5 and geminal hydrogens on C-10. The fluorine magnetic resonance spectrum of 5,5,10,10-tetrafluorodispiro[3.1.3.1]decane was a single sharp line which establishes that through-space coupling between geminal fluorines at C-5 and C-10 and geminal hydrogens on other carbons does not exist. A study of the infrared and ultraviolet spectra of dispiro[3.1.3.1]-decan-5,10-dione indicate the cross-ring carbonyl groups interact significantly.

INTRODUCTION

Proton and fluorine magnetic resonance spectra clearly show cross-ring proton-fluorine long-range coupling in substituted 3-hydro-1-fluorocyclobut-1-enes or substituted 3-fluoro-1-hydrocyclobutenes [1]. The

mechanism of the coupling is not clear and may involve above and below plane distribution of pi electrons of the planar cyclobutene ring. The unique structure of the dispiro[3.1.3.1]decane molecule forces the central four-membered cyclobutane ring to be planar. The planarity of this central ring was our rationale to synthesize 5-fluoro and 10-fluorodispiro[3.1.3.1]decane derivatives for proton and fluorine magnetic resonance studies. By using a geometrically rigid cyclobutane ring we hoped to obtain insight into through-space proton and fluorine coupling. The system might also shed information on angular dependence of coupling and indirectly on the role of pi electrons in cross-ring coupling in cyclobutenes.

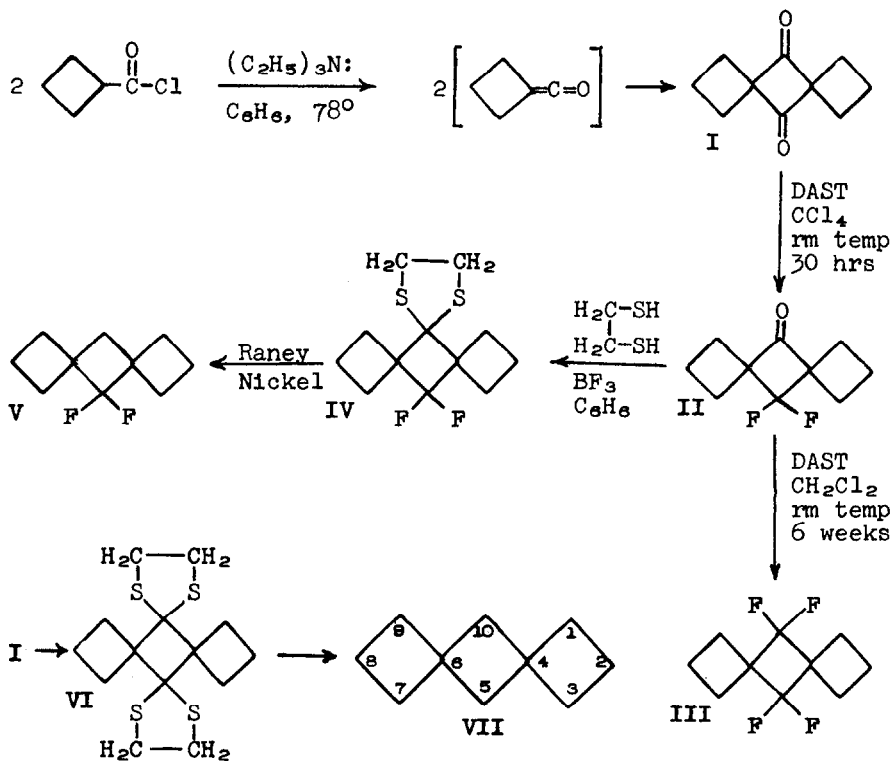
In this paper we report the selective fluorination of dispiro[3.1.3.1]decan-5,10-dione (I) by diethylaminosulfur trifluoride (DAST) [2] to give 10,10-difluorodispiro[3.1.3.1]decan-5-one (II) and the further reaction of II with DAST to form 5,5,10,10-tetrafluorodispiro[3.1.3.1]decane (III). Difluoromonoketone II was reduced to 5,5-difluorodispiro[3.1.3.1]decane. The previously reported reduction of diketone I to dispiro[3.1.3.1]decane [3] was repeated to obtain a sample for reference purposes. Mass spectra, infrared spectra, ultraviolet spectra and proton and fluorine magnetic resonance spectra were obtained as appropriate for study of cross-ring interactions.

## RESULTS AND DISCUSSION

The scheme of synthetic work carried out in this study is concisely summarized in Chart A. Dispirodiketone I was synthesized according to the procedure of Buchman [3]. Dispirodiketone I was reacted at room temperature for thirty hours with a stoichiometric amount of DAST in carbon tetrachloride solution to give after distillation a 61% yield of difluoroketone II. Reaction of difluoroketone II with excess DAST in dichloromethane for six weeks at room temperature gave the tetrafluorodispiro compound III in 60% yield.

Reduction of difluoroketone II to the corresponding dihydro compound was achieved in two steps. Difluoroketone II reacted with 1,2-ethanedithiol in benzene ( $\text{BF}_3$  catalyst) to give the thioetal, 5,5-difluoro-10,10-(1,4-dithiabutano)dispiro[3.1.3.1]decane (IV). Reduction of IV with Raney Nickel gave the desired 5,5-difluorodispiro[3.1.3.1]decane (V). The attempted direct reduction of II to V by the Wolff-Kishner reaction gave ring opening and formed products which were not identified. Sodium borohydride did not reduce or react with the tosylhydrazone of II when the procedure of

CHART A - Scheme of Synthetic Reactions



[Compound I was converted to VI and then to VII by methods used for II→IV→V]

[The numbering system for dispiro[3.1.3.1]decane system is shown for VII.]

Caglioti [4] was used. Dispiro[3.1.3.1]decane, the parent hydrocarbon of the compounds investigated, was synthesized by Buchman's method [3] for use as a reference compound for proton NMR spectra. Diketone I reacted with 1,2-ethanedithiol to form the bis-thioacetal, 5,5,10,10-bis(1,4-dithiabutano) dispiro[3.1.3.1]-decane (VI). Raney Nickel reduction of VI gave dispiro [3.1.3.1]decane (VII). The proton NMR spectrum of VII in  $\text{CDCl}_3$  was complex in the region  $\delta = 1.4$ -2.4 but had three very narrow sharp peaks at  $\delta = 1.84$ , 1.88, and 1.92 in an approximate ratio of 1:1:2 (4H:4H:8H); the proton NMR spectrum is consistent with the case where spin-spin coupling constants are greater than chemical shifts. The proton NMR spectrum of VII made analysis of the NMR spectra of I, II, III, and V much easier.

The proton NMR spectra for compounds I, II, III, V and VII from this study and VIII and IX from earlier work [5] are summarized in Table 1 where three-dimensional drawings are also presented. Although the parent hydrocarbon VII is highly symmetrical, the spectrum of VII is complex because  $J_{H-H} \geq \delta$ . In contrast the spectra of symmetrically substituted I, III and VIII are easily analyzed. The unsymmetrically substituted II, V, and IX have complex proton NMR spectra. The fluorine NMR spectra of II, III, and V are of the most importance for this work; all have singlet fluorine absorptions except possibly for V which shows very weak coupling ( $J_{H-F} < 0.5 \text{ Hz}$ ) which may be the sought after cross-ring coupling. Singlet fluorine peaks observed for II ( $w_1 = 5.0 \text{ Hz}$ ) and III ( $w_1 = 3.0 \text{ Hz}$ ) show that there is not through-space coupling between fluorines on C-5 or C-10 and protons on C-1, C-3, C-7 and C-9. The observed multiplet with  $J_{H-F} < 0.5 \text{ Hz}$  in V has an undetermined multiplicity; the source of the very weak coupling cannot be assigned. If cross-ring coupling exists in V between geminal fluorines on C-5 and geminal hydrogens on C-10, it is much weaker than the strong cross-ring coupling in fluorinated cyclobutenes [1]. On this basis it can be suggested that pi-electrons are involved in the observed long-range couplings in fluorinated cyclobutenes [1].

The mass spectra of compounds I, II, III, V, and VII show predominate cleavage across the central ring of the dispirodecane structure to give fragments as illustrated in Table 2. The other common fragment is loss of a terminal cyclobutane ring as  $C_4H_6^+$ ,  $m/e = 54$ . The fragmentation pattern observed in the mass spectrograph agrees with what is expected on the basis of kinetics and thermodynamics [6]. The data suggest that pyrolysis of III would be a useful synthetic method for preparation of 5,5-difluoromethyl-enecyclobutane.

The infrared spectrum of difluoromonoketone V shows normal cyclobutanone absorption at  $1780 \text{ cm}^{-1}$  [7]: cyclobutanone,  $1775 \text{ cm}^{-1}$  [8]; phenylcyclobutanone,  $1790 \text{ cm}^{-1}$  [9]; 3-methylenecyclobutanone,  $1770 \text{ cm}^{-1}$  [10]; 2-fluoro-2-chloro-3-(cyclohex-1-enyl)-cyclobutenone,  $1776 \text{ cm}^{-1}$  [11]. In contrast, the carbonyl absorption of diketone I occurs at  $1735 \text{ cm}^{-1}$  in the infrared. Similarly substituted 1,3-cyclobutandiones absorb in a narrow range of lower frequencies in the infrared: 2,2,4,4-tetramethylcyclobutan-1,3-dione(X),  $1725 \text{ cm}^{-1}$  [12]; dispiro[5.1.5.1]tetradecan-7,14-dione (XI),  $1735 \text{ cm}^{-1}$  [13]. The lower frequency carbonyl absorption of these similar compounds suggested to us that cross-ring conjugation between carbonyl groups exists. This postulate was confirmed by the observed ultra-

TABLE 1. Proton NMR spectra of dispiro[3.1.3.1]decane compounds

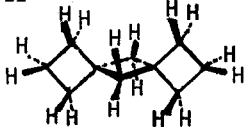
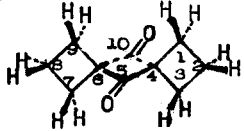
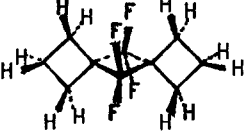
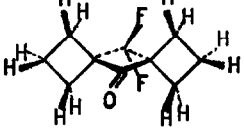
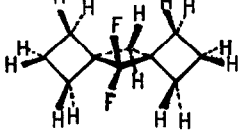
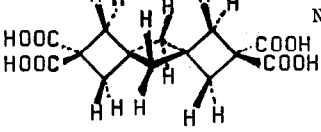
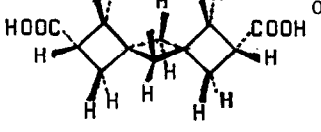

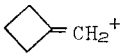
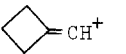
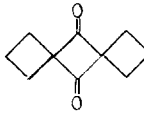
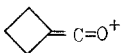
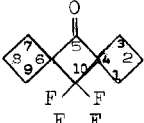
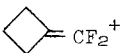
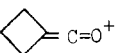

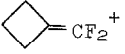
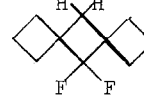
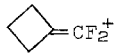
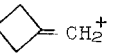
COMPOUND	Chemical shifts, coupling constants, multiplicities or protons on specified carbons.		
	on C-2 & C-8	on C-5 & C-10	C-1,C-9/C-3,C-7
VII 	Singlet ( $W_{1/2} = 1.5$ ) $\delta = 1.88$ (4H) Entire pattern of spectrum in the range $\delta = 1.4$ - $2.4$ (in $CDCl_3$ )	Singlet ( $W_{1/2} = 3.0$ ) $\delta = 1.84$ (4H) $J_{H-H} \geq \delta$  ( $W_{1/2}$ is peak width in Hz at half-height)	Singlet ( $W_{1/2} = 1.5$ ) $\delta = 1.92$ (8H), part of complex pattern where $J_{H-H} \geq \delta$
I 	Pentet at $\delta = 1.90$ (4H) $J_{H-H} = 7.5$ Hz (in $CDCl_3$ )	C=O groups at C-5 & C-10. Only two kinds of protons in compound.	Triplet at $\delta = 2.4$ (8H) $J_{H-H} = 7.5$ Hz
III 	Pentet at $\delta = 1.84$ (4H) $J_{H-H} = 7.7$ Hz (in $CDCl_3$ )	$CF_2$ groups at C-5 & C-10. Only two kinds of protons.	Triplet at $\delta = 2.18$ (8H) $J_{H-H} = 7.7$ Hz
II 	Multiplet, $\delta = 1.6$ - $2.6$ Spectrum is very complex. $J_{H-H} \geq \delta$ (in $CDCl_3$ )	C=O at C-5 and $CF_2$ at C-10 make geminal protons at C-1, C-2, C-3 and C-7, C-8, C-9 NONEQUIVALENT	Singlet of F absorption: III, $\delta = 119.1$ ( $W_{1/2} = 3.0$ ); II, $\delta = 121.4$ ( $W_{1/2} = 5.0$ ); V, $\delta = 117.0$ ( $W_{1/2} = 117.0$ ); For $CFCl_3$ , $\delta = 0$ . Multiplet, $\delta = 1.6$ - $2.6$ The spectrum is not subject to first order analysis.
V 	Multiplet, $\delta = 1.6$ - $2.1$ contains 10 H. 4H of 10H are on C-2 & C-8 and are NONEQUIV. (in $CDCl_3$ )	$CF_2$ at C-5 makes geminal protons at C-1, C-2, C-3, C-7, C-8, C-9 NONEQUIV. C-10 $CH_2$ , $\delta = 1.6$ - $2.1$	Multiplet (4H) $\delta = 1.6$ - $2.1$ Multiplet (4H) $\delta = 2.1$ - $2.7$ These are 4H closest to $CF_2$ , C-1, C-3, C-7, C-9
VIII 	C(COOH) <sub>2</sub> group No H at C-2 or C-8.	Singlet, $\delta = 2.2$ (4H) (in $D_2O$ or acetone-d <sub>6</sub> )	Singlet, $\delta = 2.7$ (8H)
IX 	CH(COOH) Only one H on C-2 & C-8. Multiplet at $\delta = 2.82$ (in NaOD/ $D_2O$ )	Singlet. Overlap makes assignment uncertain. $\delta = 2.18$ Absorption from $\delta = 1.8$ - $2.3$	Multiplet, AA'BCC' at $\delta = 2.1$ $J_{H-H} \geq \delta$

TABLE 2. Mass-spectral fragmentation data on Dispiro[3.1.3.1]-decane and 5- and/or -10 substituted derivatives

Compound designation and structure	Parent Peak (intensity) [MW, daltons]	Intensity of $C_4H_6^+$ , [54 daltons]	Other major fragments: mass (intensity)
VII 	136 (0.7) [136.2]	(14)	 $CH_2^+$  $CH^+$ 68 (49) 67 (100)
I 	164 (34) [164.2]	(50)	 $C=O^+$ 82 (100)
II 	186 (25) [186.2]	(17)	 $CF_2^+$  $C=O^+$ 104 (2) 82 (100)
III 	208 (8) [208.2]	(45)	 $CF_2^+$ 104 (100)
V 	172 (4) [172.2]	(24)	 $CF_2^+$  $CH_2^+$ 104 (73) 68 (64) Mass 67 (100)

violet spectra of compounds I, X, and XI which were observed to have the expected  $n-\pi^*$  absorptions between 260 and 360 nm. In addition, maxima were observed as follows [compound, wavelength (nm), (extinction coefficient)] in cyclohexane or ethanol solvents: I, 235 (299), 192 (~3650); X, 225 (170), 199 (~191); XI, 245 (194), 201 (~907). [Approximate values for extinction coefficients are given because of solvent cut-off.] The absorptions around 230 nm and 200 nm are probably the two expected  $\pi-\pi^*$  absorptions. The ultraviolet spectrum of cyclobutanone itself has the  $\pi-\pi^*$  absorption at 155 nm [14, 15]. Difluoromonoketone II has ultraviolet absorptions similar to those of cyclobutanone itself: [wavelength (extinction coefficient), transition]; 240→360 (<20),  $n-\pi^*$ ; 193 (~2300),  $n'-\pi^*$ ; the  $\pi-\pi^*$  absorption of II is beyond the detection range of the Cary 14. Discussion of infrared and ultraviolet spectra of I, II, X, and XI will be deferred until Raman and vacuum ultraviolet spectra are obtained. We interpret the available data to show cross-ring carbonyl conjugation in I, X, and XI.

In order to determine the generality of the selectivity of DAST, we have attempted to selectively difluorinate X and XI by DAST at 25° in dichloromethane. As determined by gas chromatography the reactions are very slow. After 60 days conversion of X is <10% and XI is 30%. Studies continue.

#### EXPERIMENTAL

Fluorinations were carried out in a polyethylene bottle. Proton magnetic resonance spectra were recorded on a Varian 220 or 90 MHz instrument. Fluorine-19 spectra were recorded on a JEOL PS-100 spectrometer; <sup>19</sup>F NMR chemical shifts were measured with an internal 4-fluorotoluene reference and corrected to trifluorochloromethane standard by adding 119.3 [17] to observed shifts. Infrared and ultraviolet spectra were recorded on Perkin-Elmer 621 and Cary 14 model spectrophotometers, respectively. Mass spectra were obtained at 15 and 70 eV on a Hitachi Perkin-Elmer RMU-6E spectrometer but are reported here only for 70 eV. Vapor phase chromatography was accomplished with a Hewlett-Packard 5730-A flame ionization chromatograph on a 6 ft. x 1/4 in. column with 3% XE-60 on 80/100 Chromosorb W. Diethylaminosulfur trifluoride (DAST reagent) was prepared as described in the literature [2]. Compounds denoted by "nc" [3] have never been abstracted by Chemical Abstracts and appear only in Reference 3, a relatively inaccessible document.

#### Dispiro [3.1.3.1] decan-5,10-dione (I) 'nc' [3]

Compound I of mp 85-86° was prepared in 39% yield from cyclobutanecarbonyl chloride (Aldrich C9, 570-6) by the method of Buchman [3]. Because the published reference is relatively inaccessible, an edited abbreviated version of the original reference is repeated here. "To a solution of 20 g (0.20 mol) of sodium-dried distilled triethylamine in 100 ml sodium-dried reagent benzene was added rapidly 21.2 g (0.18 mol) of distilled phosphorus-free cyclobutanecarbonyl chloride. The yellow slurry was heated under reflux and stirred for two hours. Due to precipitated triethylammonium chloride, the reaction mixture was quite viscous at the end of the reaction. After cooling the reaction mixture was poured with stirring into a mixture of 50 ml conc HCl and 300 g ice. The benzene layer was separated, washed once with water, and concentrated in vacuo. A brown oily residue remained which crystallized on standing. Crystallization from ligroin (30-60°) and work-up

of mother liquors gave 6.0 g (.037 mol, 40%), mp 83-85°. Recrystallization from petroleum ether gave an analytical sample mp 86.0-86.5°. Analysis: Found: C, 73.05; H, 7.45%.  $C_{10}H_{12}O_2$  requires C, 73.14; H, 7.37%."

The spectral properties of I are reported here for the first time on a sample of I mp 85-86°. IR ( $CCl_4$ ) 2995 and 2940 (s) (C-H), 1735 (vs) (C=O), 1270 (s), 1205 (m), and 1065 (w)  $cm^{-1}$ ;  $^1H$  NMR 90MHz ( $CDCl_3$ )  $\delta$  = 1.90 (p,  $J$  = 7.5Hz, 2 sets 2H), 2.4 (t,  $J$  = 7.5Hz, 2 sets of 4 H); Mass Spectrum m/e (relative intensity) 164(34), 136(3), 135(10), 121(5), 108(32), 93(13), 82(100), 80(26), 79(30), 55(26), 54(50), 53(38).

10,10-Difluorodispiro [3.1.3.1] decan-5-one (II). nc

To 14.8g (0.0902 mol) I in 45 ml  $CCl_4$  at 25° was added 11.3 ml (0.0902 mol) DAST. The reaction was stirred for 30 h, then poured into water, extracted with ether and dried ( $MgSO_4$ ). Distillation gave 10.3g (61%) II, bp 55° (4.2 mm). VPC analysis showed II to be ca. 97% with 1-2% each of I and III. The retention times for IX, II, and I at 108° were 1.0, 2.0, and 9.0 min, respectively. A pure sample of II was obtained by column chromatography on silica gel with pentane as the eluent. The spectral properties of II are: IR ( $CCl_4$ ) 2995 and 2945 (s) (C-H), 1780 (vs) (C=O), 1428 (w), 1300 (s) (C-F), 1270 (s), 1160 (s), 1110 (s), and 1020 (m)  $cm^{-1}$ ;  $^1H$  NMR 90MHz ( $CDCl_3$ )  $\delta$  = 1.6-2.6(m);  $^{19}F$  NMR 90MHz ( $CDCl_3$ ),  $\delta$  = 121.4,  $W_{\frac{1}{2}}$  = 5.0 Hz. Mass spectrum, m/e (relative intensity) 186(25), 158(70), 143(6), 130(13), 111(13), 82(100), 54(17). Analysis: Found: C, 64.48; H, 6.69; F, 20.30%.  $C_{10}H_{12}F_2O$  requires C, 64.51; H, 6.50 F, 20.41%.

5,5,10,10-Tetrafluorodispiro [3.1.3.1] decane (III). nc

To 6.90g (0.0371 mol) II in 20 ml  $CH_2Cl_2$  at 25° was added 6.0 ml (0.0480 mol) DAST. The reaction was stirred for six weeks and then worked up as described for the preparation of II above. Distillation bp 58-59° (14 mm) gave 4.6g (60%) of 97% pure III with the following spectral properties: IR ( $CCl_4$ ) 3000 and 2960 (s) (C-H), 1300 (s) (C-F), 1250 (m), 1200 (s), 1075 (s), 1040 (s), 970 (m) and 925 (w)  $cm^{-1}$ ;  $^1H$  NMR 220MHz ( $CDCl_3$ )  $\delta$  = 1.87 (p,  $J$ =7.7Hz, 8H), 2.18(t,  $J$ =7.7Hz,  $^{19}F$  NMR 94MHz ( $CDCl_3$ )  $\delta$  = 119.1,  $W_{\frac{1}{2}}$  = 3.0 Hz. Mass Spectrum m/e (relative intensity) 208(8), 193(11), 188(5), 180(56), 165(37), 161(45), 152(24), 147(17), 111(24), 104(100), 97(21), 85(10), 54(45). Analysis: Found: C, 57.98; H, 5.97; F, 36.14%.  $C_{10}H_{12}F_4$  requires C, 57.89; H, 5.84; F, 36.01%.



5,5-Difluorodispiro[3.1.3.1]decane (V) from II via 5,5-difluoro-10,10-(1,4-dithiabutano)dispiro[3.1.3.1]decane (IV). V, nc; IV, nc

To 1.00 g (5.37 mmol) II and 1.6 ml 1,2-ethanedithiol in 20 ml benzene was added 5.0 ml 98% boron trifluoride in ether. The reaction mixture was stirred overnight at room temperature and then heated to 50° for 30 min. Ether (50 ml) was added to the cooled mixture which was then extracted three times with 20-ml portions of 10% sodium hydroxide solution. The organic layer was dried (MgSO<sub>4</sub>) and the solvent removed at reduced pressure. To 0.500 g (1.91 mmol) of the ethylene thioetal product IV in 26 ml ethanol was added 4 teaspoons full of Raney nickel catalyst [16] which was deactivated by refluxing in acetone for one hour. The mixture was heated to 60° for three days, then poured into water, extracted with ether, dried (MgSO<sub>4</sub>) and distilled to give 0.26 g V, bp 60°(30 mm). Compound V had the following spectral properties: IR (neat) 2985 and 2940 (s) (C-H), 1445 (m), 1315 (s) (C-F), 1245 (m), 1195 (w), 1160 (w), 1120 (s), 1080 (s), 1020 (s), 980 (m) and 920 (w) cm<sup>-1</sup>; <sup>1</sup>H NMR 90 MHz (CDCl<sub>3</sub>) δ = 1.6-2.1(m, 10H), 2.1-2.7(m, 4 H); <sup>1</sup>F NMR 94 MHz (CDCl<sub>3</sub>) δ = 117.0, W<sub>1/2</sub> = 6.5 Hz, observed as a singlet with fine structure, J = 0.5Hz; Mass Spectrum m/e (relative intensity) 172(4), 157(5), 144(24), 143(15), 130(17), 129(50), 124(9), 118(10), 117(13), 116(38), 115(38), 111(11), 109(21), 108(15), 104(73), 103(20), 93(26), 91(14), 81(10), 80(27), 79(38), 71(14), 69(27), 68(64), 67(100), 65(15), 57(17), 55(24), 53(32), 51(15), 43(30), 42(10), 41(48), 40(54), 39(45), 28(49).

Dispiro[3.1.3.1]decane (VII). "nc" [3]

Compound VII was synthesized from compound I by the method described by Buchman [3]. The only change was to substitute 1,2-ethanedithiol for methyl sulfide. The procedure described earlier in this paper was used to convert I into 5,5,10,10-bis(1,4-dithiabutano)-dispiro[3.1.3.1]decane (VI). VI was then reduced with Raney Nickel to VII. Spectral properties not reported earlier for VII are: IR (CCl<sub>4</sub>) (neat) 2995 and 2940 (s), 1422 (m), 1325 (w), 1375 (m), 1150, 1085, and 910 (w), and 790 (m); <sup>1</sup>H NMR (CCl<sub>4</sub>) 90 MHz δ = 1.6-2.0, multiplet; Mass Spectrum m/e (relative intensity) 136(0.7), 122(1), 121(8), 110(8), 108(29), 107(35), 95(30), 94(14), 93(99),

91(27), 82(20), 81(25), 80(42), 79(86), 78(8), 77(27), 70(10), 69(33), 68(49), 67(100), 66(16), 65(10), 56(12), 55(36), 54(14), 53(26), 51(7), 43(14), 44(9), 41(58), 40(32), 39(42), 29(17), 28(66).

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#### DEDICATION

This work is dedicated to the memory of Dr. William A. Sheppard, 1929-1979, who served as an inspiration to many of us and who first informed one of us (CMS) of the usefulness of DAST.

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